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Abstract

Effluent constituents in a complete ClO_2-substituted bleached Kraft mill were monitored in process lines and sewers for an extended period to determine the transport of these constituents through the mill and its treatment system. The principal finding was that COD and AOX (adsorbable organic halogen) concentration profiles were related at the end-of-pipe. The relationship is believed to be indirect, i.e., both parameters reflect non-biodegradable lignin residuals. Conductivity at the recovery sewer was an excellent indicator of black liquor upsets. No trisubstituted or higher chlorophenols or chlorinated dioxins or furans were found in any of the bleach line filtrates.

Introduction

The proposed "cluster rules" (1) which include revised effluent guidelines for the pulp and paper industry will lead to major capital investment by the industry. In order to derive maximum benefit from this expenditure, it is prudent to understand how effluent constituents move through the mill complex and into the environment, and to define any interrelationships among these constituents. A process or control technology change designed to reduce the concentration of a given effluent component may decrease levels of other constituents as well, and an ability to predict these dependencies will optimize capital spending. We have conducted a detailed study of effluent components at the Georgia-Pacific mill at Leaf River, MS, and in this paper, we develop and rationalize correlations among constituent profiles at various points in the mill system.

Results

Description of the Leaf River Mill

During the study, daily production at Leaf River, which pulps both hardwood and softwood, approximated 1,500 tons of bleached Kraft market pulp. The digester is a continuous Kamyr dual-vessel hydraulic unit which discharges brownstock into a blow tank. This is followed by a Kamyr pressure diffusion washer, a Kamyr two-stage diffusion washer, and a drum washer.

A single five-stage bleach line swings between hardwood and softwood. During this study, the bleaching sequence for both species consisted of ClO_2 bleaching, extraction with NaOH reinforced with O_2 and H_2O_2, ClO_2 bleaching, extraction with NaOH and H_2O_2, and final bleaching with ClO_2 ($D\text{-}E_{op}\text{-}D\text{-}E_p\text{-}D$). The nominal kappa number of the pulp (a measure of lignin) entering the bleach plant was 30 for softwood and 14 for hardwood. The bleached pulp is considered as elemental chlorine free, or "ECF".

Approximately 20 million gallons of water are taken daily from the Leaf River, treated by coagulation in a clarifier, and passed through gravity filters before process use. Only the first- and second-stage bleach filtrates are sewered; the others are used as wash water in the preceding stages.

The treatment system consists of a bar screen, two primary clarifiers with each providing a 4 hour detention, equalization, cooling, activated sludge treatment in an aeration basin, two secondary clarifiers, and a final holding pond. The equalization basin, with 10 floating aerators, has a surface area of 237,864 square feet and a detention time of 16.5 hours. Ammonia and phosphoric acid are added after equalization, and the wastewater flows to a cooling tower which discharges to a 48-million gallon aeration basin with a 45 hour detention. The flow is then divided between two 215-foot diameter secondary clarifiers, each with a detention time of 9.4 hours. Approximately 8 MGD (40%) of the secondary sludge is recycled to the aeration basin. The secondary clarifiers lead to a holding pond which discharges continuously through diffusers to the Leaf River. The typical detention time for the holding pond is approximately 3-12 days.

Description of the Analytical Effort

In order to capture seasonal variability, 10 sampling episodes were conducted during August/September 1993, followed by eight in February 1994. Six grab samples were taken over a 24-hour period and composited where appropriate. Water flow was estimated for the acid sewer, acid filtrate, and alkaline filtrate; it was measured with flow meters for all the other points sampled.

The sampling plan is provided in Table 1. Some of the summer analyses were discontinued in the winter event since the analytes were not detected in any of the summer episodes. Since the acid filtrate and the acid sewer gave very similar results for all the analytes considered, sampling of the acid filtrate was discontinued in the winter. Chlorophenols were dropped from the waste treatment influent and effluent, and acrolein analysis was discontinued completely since these analytes were not observed in the summer. Useful resin acid data could not be obtained for the summer sampling due to analytical difficulties. These were resolved before the winter event.

Chlorophenol analysis by EPA method 1653 (2) was limited to the following congeners: 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol, 3,4,6-tri-chloro-guaiacol, 3,4,5-trichloroguaiacol, 4,5,6-trichloroguaiacol, tetrachloroguaiacol, 3,4,6-trichlorocatechol, 3,4,5-trichlorocatechol, tetrachlorocatechol, trichlorosyringol. The lower congeners were not determined since they are consumed in

the treatment system. Analysis of volatiles by EPA method 624 (3) was restricted to methylene chloride, acetone, chloroform, 2-butanone, and acrolein (summer only).

A full-scale dioxin analysis by NCASI method 551 (4) was run on the acid and alkaline bleach line filtrates taken during episode 1. No 2378-tetrachlorodioxin/furan (TCDD/F) was detected, but octachlorodibenzodioxin was found at 0.06 ppt in the ALF sample (detection limit 0.02 ppt). A single 2378-TCDD/F scan run on the ALF sample taken during episode 11 led to non-detects, which was consistent with previous results. Methanol was determined by EPA method 8015A (5), AOX by EPA method 1650A, and resin acids by NCASI method 501 (6).

TOC, DOC, and color were determined at the Leaf River facility. BOD, conductivity, and TSS were determined at Bonner Analytical Testing Company, Hattiesburg, MS. 2,3,7,8-TCDD, 2,3,7,8-TCDF, and AOX were determined at Triangle Laboratories, Durham, NC. Six sets of samples taken each day for three episodes were sent to S-Cubed for analysis of volatiles by method 1624. All other analyses were conducted at Ecology and Environment Inc., Buffalo, NY. Two samples, ACF episode 13, and ALF episode 15, were sent to ETL EnviroTest, Edmonton, Canada, for chlorophenol analysis for an independent cross-validation.

Major Analytical Findings

Chlorophenols were not detected in any of the samples taken with the exception of 2,4,6-trichlorophenol which appeared at unquantifiable trace levels in the single ACF sample used for cross-validation. Other analytes that were not found were dichlorodehydroabietic acid (all locations); neoabietic acid (ALF, ACS); methanol (WTE), 2-butanone (WTE), 14-chlorodehydroabietic acid (ACS, PMS, RCS, EVS, WTI, WTE); 12-chlorodehydroabietic acid (ACS, PMS, RCS, EVS). Most of the acetone determinations in method 1624 did not meet QC criteria due to interference from thiobismethane present in the sample. Foaming was observed for many of the samples, and this was believed to contribute to difficulties with acetone and 2-butanone.

Discussion

Linear regressions were run for each analyte profile *vs.* every other analyte profile, and the most significant of these from an environmental perspective are listed in Table 2. By far the most important relationship is that between end-of-pipe (WTE) AOX and COD, whose concentration profiles are illustrated in Figures 1 and 2, respectively. Since AOX concentrations are two orders of magnitude below COD levels, the correlation cannot reflect the same constituent. Rather, both COD and AOX are expressions of the non-

biodegradable components of the end-of-pipe effluent. In other words, since end-of-pipe AOX does not biodegrade in the treatment system, it should correlate with other constituents in the process that also do not biodegrade, such as end-of-pipe COD. Both parameters reflect lignin residuals, which is related to the amount of lignin removed. In other words, the levels of the two constituents rise and fall in tandem as the amount of lignin processed changes. Importantly, the AOX-COD relationship at the WTI (inlet to the treatment system) is poor because the COD at the inlet contains much more biodegradable material than does the AOX; i.e., the AOX-COD relationship only emerges at the end-of-pipe after the biodegradable components are removed.

The generality of the AOX-COD relationship can be appreciated from the data in Table 3 for end-of-pipe [AOX]/[COD] and [AOX]/[TOC] ratios at Leaf River and the Georgia-Pacific mill at Brunswick, GA. Since end-of-pipe [COD] and [TOC] are related (Table 2), the two ratios measure similar effects. The first entry in Table 3 represents data collected in this study. The second reflects data routinely obtained from the Leaf River mill. The third is from measurements taken at Brunswick. The Brunswick mill pulps mainly softwood and uses an aeration stabilization basin. Leaf River swings between hardwood and softwood and uses an activated sludge system. The constancy of the ratios over time and across two different mills with different operating practices clearly demonstrates the link between AOX and organic carbon at the end-of-pipe. Most of the COD at Leaf River originates from the bleaching process; e.g., half of the COD entering the influent to waste treatment in the first episode originated from the acid and alkaline sewers. This situation reflects a clean well-run mill; presumably, the relationship would not be as good if COD entered the system from sources other than the bleach plant, e.g. from a spill. We also emphasize that both Brunswick and Leaf River use the same bleaching sequence; a stable [AOX]/[COD] ratio may not necessarily follow from other bleaching sequences.

Chloroform at the acid sewer (ACS) was well correlated ($r=0.92$) with that in the treatment system influent (WTI). However, as shown in Figures 3 and 4, there is a 53% increase in chloroform as it enters the waste treatment system from the acid sewer. This effect has been noted before (7,8) and probably originates from the mixing of the acid and alkaline streams just before the influent. The AOX in the acid stream is a complex mixture of chloroorganics, some of which bear trichloromethyl-α-carbonyl groups. Upon mixing with the alkaline stream, these groups are probably converted to chloroform through the haloform reaction.

The excellent correlation (r=0.997) between COD and BOD in the pulp mill sewer (PMS) indicates that COD from this source is biodegradable. This is not surprising since much of the carbon load in this stream derives from resin acids and other relatively labile lignin-derived material, as compared to material from the bleaching stages which is more difficult to extract. Similar reasoning applies to the relatively good BOD-COD relationship in the evaporator sewer.

The high r-coefficients for correlations between color and COD, TSS and conductivity at the recovery sewer (RCS) result from two unusually high values, indicating a spill. The color and conductivity profiles are illustrated in Figures 5 and 6, respectively. The relationship suggests that conductivity is a good, inexpensive indicator for black liquor spills. Color and COD correlate well at the end-of-pipe (WTE) indicating that color originates from non-biodegradable carbon. Color increases across the pond; WTE-color exceeds WTI-color by 22%. This suggests that much of the organic material in the lagoon is not mineralized, but is converted into smaller more chromophoric units. TOC and DOC correlate well across the board; e.g. PMS-TOC correlates with PMS-DOC with r=0.998 since the organic carbon in the system is mostly dissolved.

Some of the relationships were unexpected, and we are unable to propose a defensible basis. For example, ALF and WTI methanol are well correlated. Since methanol from the pulping, rather than the bleaching operation is the principal feed into the influent, this relationship is surprising. Also, the 2-butanone-acetone relationship at the evaporator is the only good 2-butanone-acetone correlation found. It might be argued that the relationship might arise from the fact that both 2-butanone and acetone are produced in pulping. In this case, a correlation of similar or better quality should be found in the pulp mill sewer. However, r=0.50 for 2-butanone *vs.* acetone in the pulp mill sewer.

The absence of chlorophenols in the bleaching lines does not preclude their presence in sludge, since hydrophobic organics concentrate in the lignin-derived components of sludge (9-11). However, no chlorophenols were found in a sample of mixed primary and secondary sludge at a detection limit of 80-170 µg/kg.

In summary, we have shown that end-of-pipe AOX and COD are semi-quantitatively related, which suggests that a process or treatment change that reduces one component should also proportionately reduce the other. We have demonstrated that chloroform is generated when the acid and alkaline streams mix, and have illustrated the utility of conductivity monitors in the

recovery sewer to monitor black liquor spills. Finally, we have shown that good correlations can be developed in the field among constituent profiles, and can be used to understand their interrelationships as the components move through the mill system.

Acknowledgments

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Captions to Figures

Figure 1: AOX profile at the waste treatment effluent
Figure 2: COD profile at the waste treatment effluent
Figure 3: Chloroform profile at the waste treatment effluent
Figure 4: Chloroform profile at the acid sewer
Figure 5: Color profile at the recovery sewer
Figure 6: Conductivity profile at the recovery sewer

Table 1: Sampling plan at Leaf River

	MPW	ACF[1]	ACS	ALF	WTI	PMS	RCS	EVS	WTE
color	x	x	x	x	x	x	x	x	x
pH	x	x	x	x	x	x	x	x	x
conduc-tivity	x	x	x	x	x	x	x	x	x
TSS	x				x	x	x		x
COD	x	x	x	x	x	x	x	x	x
DOC	x	x	x	x	x	x	x	x	x
TOC	x	x	x	x	x	x	x	x	x
AOX	x	x	x	x	x				x
BOD	x				x	x		x	x
resin acids	x		x	x	x	x	x	x	x
methanol	x	x	x	x	x	x	x	x	x
chloro-phenols	x	x	x	x	x				x
volatiles	x	x	x	x	x	x		x	x
TCDD/F[2]		x		x					

[1]dropped for the winter sampling; [2]episodes 1 and 11 only

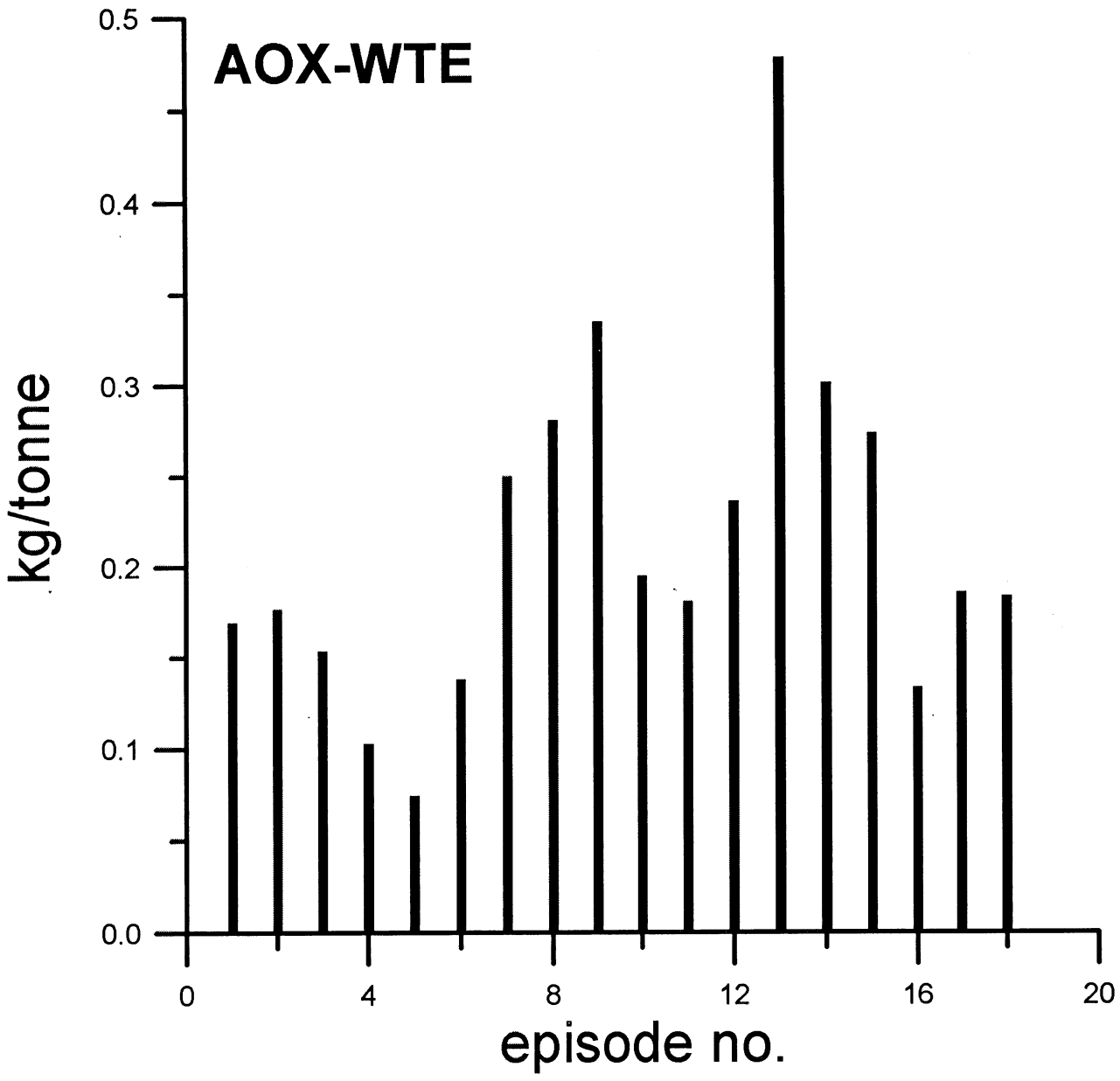
MPW: mill process water; ACF: acid filtrate; ACS: acid sewer; ALF: alkaline filtrate; WTI: waste treatment influent; PMS: pulp mill sewer; RCS: recovery sewer; EVS: evaporator sewer; WTE: waste treatment effluent; CSI: condensate stripper inlet; CSO: condensate stripper outlet

Table 2: Relationships Between Contstituent Profiles at Leaf River

analyte-1	analyte(s)-2	r
PMS-COD	PMS-BOD (or DOC)	0.997
EVS-acetone	EVS-2-butanone	0.99
RCS-color	RCS-conductivity (or COD or TSS)	0.92-0.994
ALF-MeOH	WTI-MeOH	0.94
WTE-color	WTE-COD	0.92
ACS-$CHCl_3$	WTI-$CHCl_3$	0.92
EVS-BOD	EVS-COD	0.84
WTE-COD	WTE-AOX	0.82
WTE-TOC	WTE-COD	0.80
WTI-AOX	WTI-TOC (or DOC)	0.78
WTE-BOD	WTE-resin acids	0.75-.78
WTI-AOX	WTI-COD	0.53

Table 3: Constancy of [AOX]/[COD] and [AOX]/[TOC]

	[AOX]/[COD]	[AOX]/[TOC]	Period
Leaf River	0.0071 (σ=0.0016) n=18	0.0198 (σ=0.005) n=18	8.26.93 - 2.25.94
Leaf River		0.0214 (σ=0.0007) n=65	8.25.93 - 9.8.94
Bruns-wick	0.0057 (σ=0.0003) n=5		8.10.94 - 8.14.94


AOX-WTE
kg/tonne
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0.3
0.2
0.1
0.0
0
4
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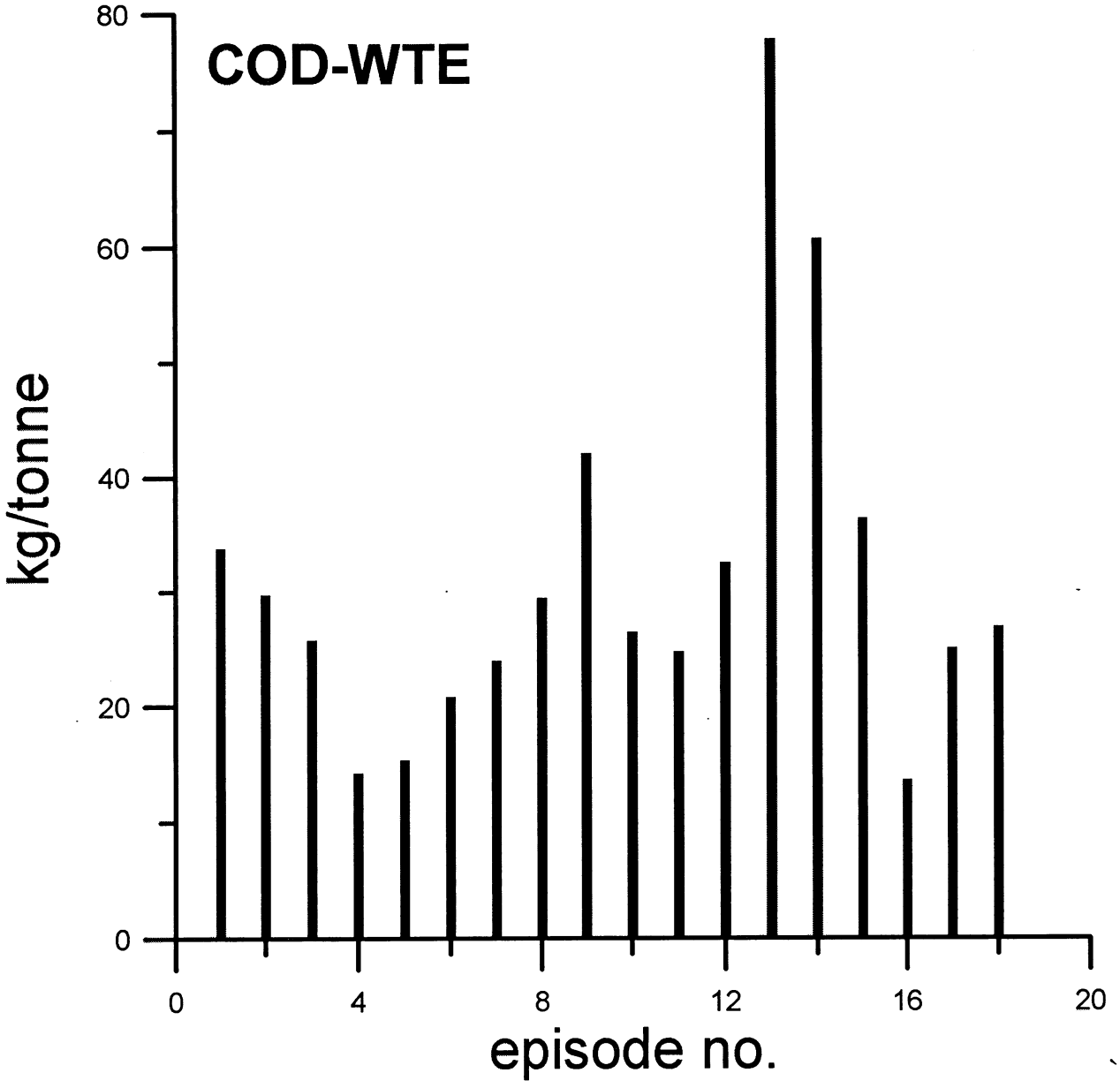
12
16
20
episode no.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kg/tonne
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16
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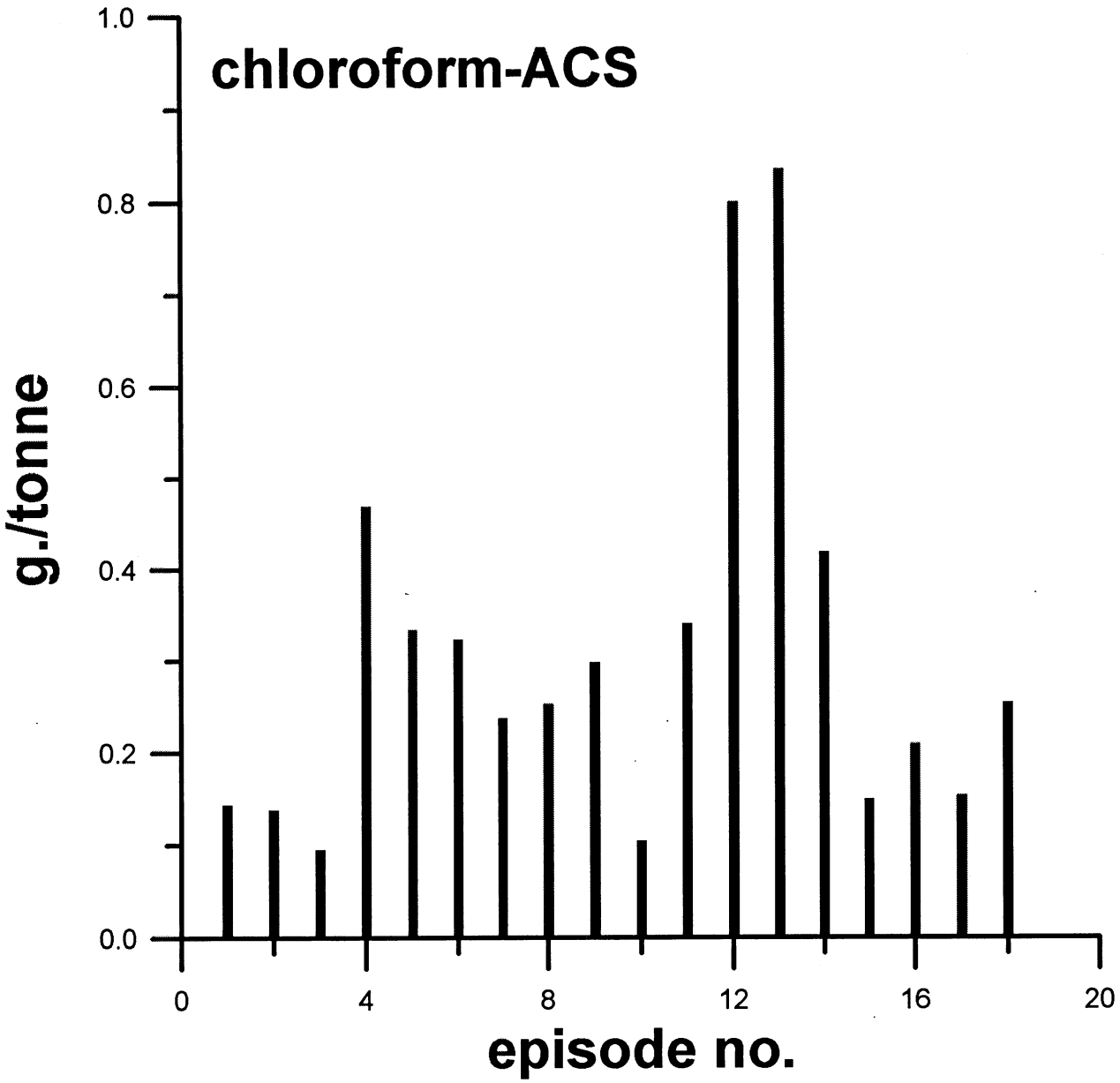
chloroform-ACS
g./tonne
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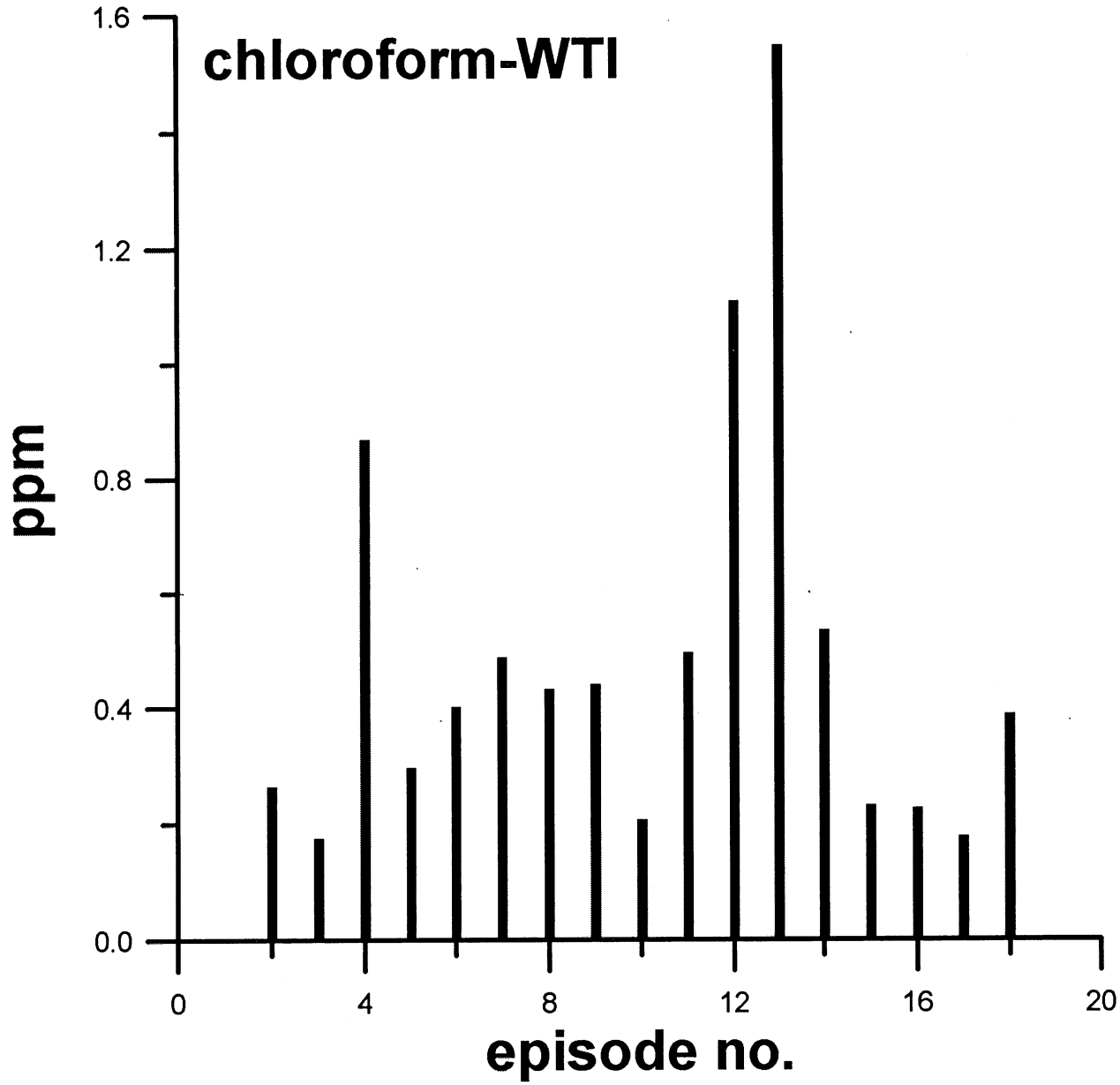
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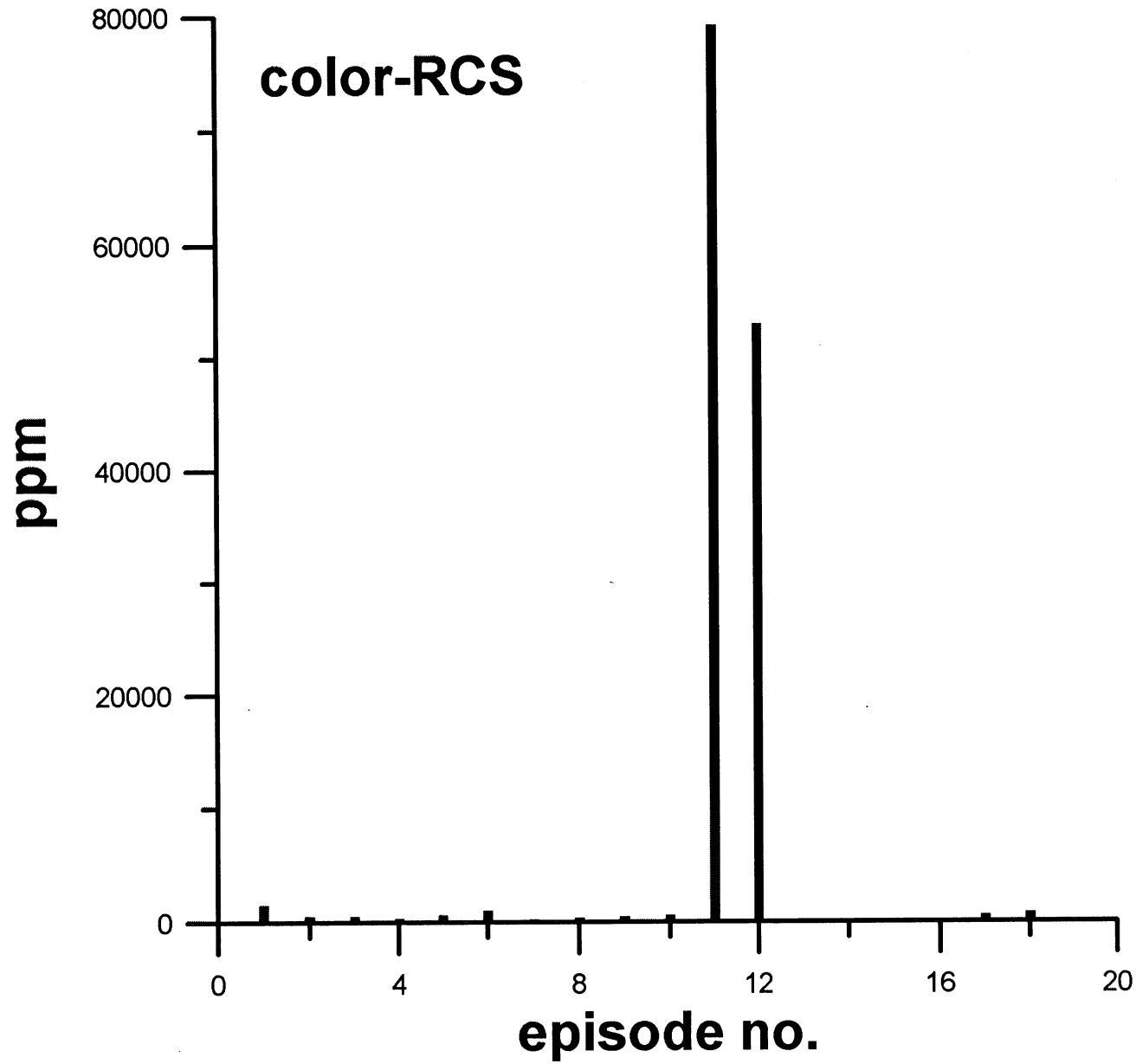
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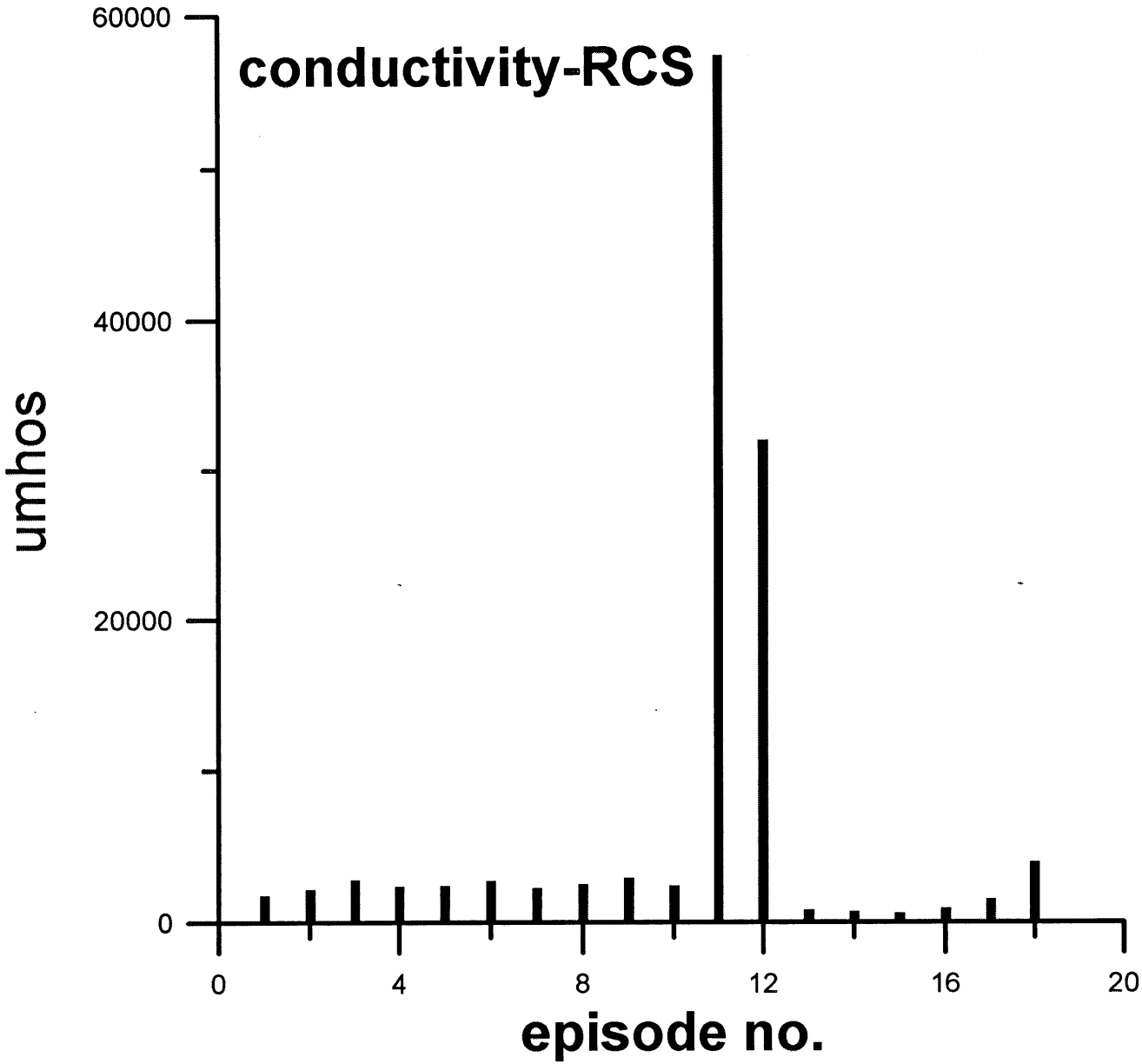
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